SUDBURY ENVIRONMENTAL STUDY

ATMOSPHERIC RESEARCH PROGRAM: A SYNOPSIS

SES 010/82

FALL 1982

Ontario
Ministry of the Environment

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Minister

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Deputy Minister

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October 1982

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SES 010/82
ISBN 0-7743-7547-7
ARB-27-82-ARSP

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ACKNOWLEDGEMENTS

This compilation is based on results published in many reports. Appreciation is extended to all those authors and experimenters whose devoted efforts have made this possible. Special thanks are due to Dr. M. Lusis and Mr. R.J. Vet for their support throughout the Sudbury Environmental Study. Critical review of this account by Drs. M. Lusis, D. Balsillie and P.K. Misra (of section 6 on modeling), Messrs. R. Potvin, and V. Ozvacic (of section 3 on emissions) is gratefully acknowledged.

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1. INTRODUCTION

Sudbury, Ontario is an area of major environmental interest because of the volume of sulfur dioxide and particulates emissions due to smelting and mining activities. In 1973, the Ontario Ministry of the Environment (MOE) initiated a multi-disciplinary study to assess both the atmospheric and aquatic aspects of the problem. In the initial stages, emphasis was put on the latter aspect. Early atmospheric studies took the form of projects awarded to universities and consulting firms. As a consequence of these findings, the Air Resources Branch began an integrated program in 1977.

The objective of the Air Resources Branch program was threefold:

(1) to define the sources and source strengths of atmospheric emissions in the Sudbury Basin

(2) to determine the fate of these emissions

(3) to determine the ambient air concentrations of potentially hazardous substances.

To be more specific, the atmospheric program attempts to assess the wet and dry deposition rates of the emissions in the Sudbury Basin; to assess the contribution of imported pollutants (i.e., long range transport of air pollutants into the Sudbury Basin); and to predict the impact of changing emission rates on ambient concentrations and atmospheric deposition in the Sudbury Basin and further afield.

2. APPROACH USED IN THE STUDY

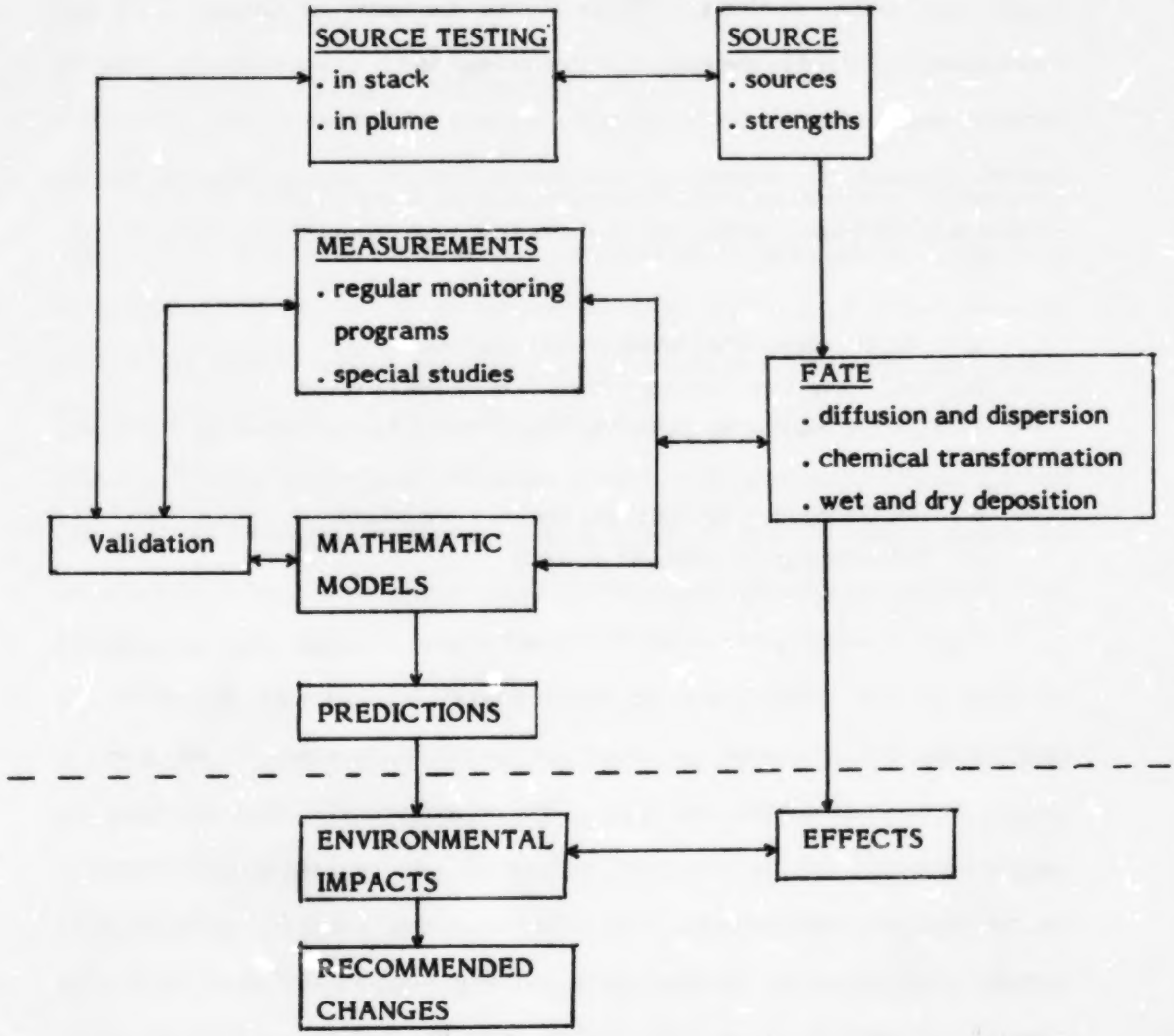
In essence, the study problem was the origin and fate of the pollutants: the nature and quantity of the emissions, and then dispersion, chemical transformation, and ultimate deposition subsequent to being released to the atmosphere. Figure 1 is a diagrammatic representation of the atmospheric portion of the study components. Information on emission rates and characteristics is obtained by stack tests or plume-level sampling near the chimney; information on the subsquent fate of the emisisons results from air and precipitation routine monitoring as well as special field studies and mathematical modelling of air quality and atmospheric deposition. Modeling and monitoring are interrelated: monitoring results are needed to provide model input parameters, while modeling aids in the interpretation of monitoring data and can be used to interpolate results between monitoring stations and to extrapolate beyond them.

In the following sections, dicussion is partitioned into:

1. Sources and source strengths
2. Regular monitoring programs
3. Supporting studies for model development
4. Mathematical modelling.

FIGURE 1:

Schematic Representation of the Atmospheric Component of the Sudbury Environmental Study



3. SOURCES AND SOURCE STRENGTHS

3.1 Sources

The major air pollution sources in the Sudbury Basin are all located within a distance of 15 km from the city of Sudbury, and are associated with two copper and nickel smelters - INCO Metals Company at Copper Cliff and Falconbridge Limited in the town of Falconbridge and a nickel refinery - iron ore recovery plant complex (INCO Metals Company at Copper Cliff). These two sources account for almost all the sulfur dioxide and particulate matter emissions in the Basin. Within the smelters five major sources can be identified:

a. INCO Copper Cliff Smelter, 381 m stack
b. INCO Iron Ore Recovery Plant (IORP) 194 m stack
c. INCO's two 45 m pelletizer plant stacks (emissions ceased in April, 1980)
d. INCO Copper Cliff Smelter, low level emissions
e. Falconbridge Smelter, 93 m stack

Prior to entering the stack mentioned above, emission gases are cleaned of most of the particulates by electrostatic precipitators sometimes in combination with cyclones, scrubbers and settling chambers. However, a portion is emitted due to less than 100% collection efficiency of these air pollution control devices. Low level emissions result from unconfined emissions and escape from various process fume collection steps. These fumes are emitted through small stacks on building roofs, building windows and ventilators. No attempts are made to scrub sulfur dioxide from the flue gases, although sulfur elimination (e.g., pyrrhotite rejection in the ore beneficiation process) and sulfur fixation (e.g., liquid SO_2 and sulfuric acid manufacturing) are the current SO_2 abatement methods employed.

Details of the sources, their strengths and composition, are given in report ARB-ETRD-09-82 (Ozvacic, 1982).

3.2 Summary of Relevant Industrial Processes

The following discussion is intended to present a summary of the relevant processes used by both INCO metals and Falconbridge Limited. A more detailed description has been published elsewhere (Fitz, 1978).

3.2.1 INCO Metals Copper Cliff Smelter Complex

The 381 m stack emits gases from pyrometallurgical smelting processes at the INCO's Copper Cliff smelter. The purpose of the smelting processes is to make nickel and copper of appropriate purity in the form of nickel bessemer matte and blister copper from suitably prepared ore concentrates. About 157,000 cubic meters of gases at a temperature of 130°C are emitted each minute. The gas temperature increases with increasing production rates and can reach 175°C when the smelter is operated at full capacity. These gases are received from various processes via two inlet breachings situated opposite each other at the stack base.

After crushing and grinding of the ore, iron sulfide is separated magnetically, while copper and nickel are concentrated by flotation. The copper concentrate is smelted in a flash furnace where the main products are copper matte and sulfur dioxide at about 80% concentration in the off-gases. These gases are air cooled in a settling chamber, scrubbed in a splash tower, treated in gas scrubbers and a mist electrostatic precipitator then sent to the sulfuric acid plant for the production of liquid sulfur dioxide. In case of emergencies, the gases may be directed to the 381 m stack via a bypass system. The gases arising from the handling operations of the two melted products, slag and copper matte are exhausted through forced draft vents to the atmosphere whereas fugitive gas emissions from the flash furnace area are released to the atmosphere, under natural draft, through large vents.

Copper matte from this furnace is sent to copper converters to reduce the sulfur content and to oxidize the iron to produce blister copper for further refining. Converting is a batch process in which oxygen enriched air is blown through the molten charge to produce oxides of iron which react with silica and form slag which floats on the top of the molten converter contents. Blister copper, the main product of converting, is sent to the copper refinery for further processing. The main portion of the converter off-gases is sent to the 381 m stack via collection fume hoods and flues. Part of these emissions escape from around the collecting hoods into the building, and are exhausted outside through roof ventilators, as fugitive emissions.

The nickel concentrate from the flotation operation is first roasted in multi-hearth roasters to remove moisture and part of the sulfur as sulfur dioxide. Heating of concentrate on the roaster hearths is accomplished by combustion of natural gas and oxidation of the iron sulfide to iron oxide in the ore with air. This air along with sulfur dioxide and entrained particulates is ducted to the 381 m stack via the No. 1 electrostatic precipitator. In addition to these confined emissions, there are periodic fugitive emissions that are vented to the atmosphere via four roof fans.

The calcine (product of roasting), is fed to reverberatory furnaces to combine iron oxide with silicate and produce slag which floats on top of the matte containing the heavier sulfides of copper, nickel and iron. Sulfur dioxide is also produced in this furnace. Combustion of oil, sustained with oxygen enriched air, provides the necessary heat to maintain the furnace contents in a molten state. The combustion gases with entrained particulates and sulfur dioxide are conveyed via a reverb-header flue to the 381 m stack after passing through boilers and electrostatic precipitator No. 4. Unconfined fugitive emissions from this furnace originate during the removal of matte and slag from the furnace. They are collected by hoods (forced draft fans) and exhausted to

the atmosphere through separate vents. In addition, emissions escaping the furnace through its brickwork during periods of increased pressure within the furnace, and the emissions originating during converter slag removal, exit the smelter building via the roof ventilators above the furnaces. There are a total of six reverberatory furnaces and the number in operation varies between two and five.

Matte from these furnaces is fed to the nickel converters where similar operations to copper converting are carried out. After oxidation of iron and formation of slag, a converter is rotated for skimming and discharging of high grade copper-nickel matte for casting and cooling. Emissions from various steps (charging, blowing, skimming and pouring) are collected by hoods and directed to electrostatic precipitators and the 381 m stack. However, part of these emissions escapes around the hoods and leaves the building via the ventilator openings. There are nineteen converters in the smelter, normally fourteen in the nickel circuit. However the arrangement for these circuits is flexible.

3.2.2 INCO Metals Iron Ore Recovery Plant and Nickel Refinery Complex

The INCO 194 m IORP (Iron Ore Recovery Plant) stack is the second largest source of industrial emissions in the Sudbury Basin. Approximately 9500 cubic meters of gas at 150°C to 200°C containing metals, sulfur dioxide and sulfuric acid are exhausted every minute from this stack. The stack receives off-gases from INCO's Iron Ore Recovery Plant, INCO's Nickel Refinery and three sulfuric acid plants. Emissions from these five plants are cleaned of the majority of entrained particulates prior to entering the stack. Cyclones, electrostatic preciptators, scrubbers, settling chambers and combustion units are used for this purpose at the Iron Ore Recovery Plant, electrostatic precipitators at the Nickel Refinery; and packed absorption towers equipped with a demister at the three plants.

There are four processes involved in iron ore recovery at the INCO plant; roasting and reduction of pyrrhotite concentrate, leaching, recovery and pelletizing. The purpose of these processes is to recover nickel from pyrrhotite concentrate received from the INCO smelter and to prepare iron rich pellets for marketing. In the roasting step, most of the sulfur is eliminated by oxidation at high temperatures. Off-gases from six fluid bed roasters are cleaned of particulate materials and sent to the acid plants. These gases could be temporarily diverted to the 194 m stack in case of upsets, however, if problems persist the plant is shut down. To facilitate the separation of nickel from iron in subsequent leaching and reduction steps, as well as to reduce the oxides of iron, the concentrate from the roasters is treated in six reduction kilns. Off-gases from these kilns are passed through shell and tube heat exchangers, cyclones, water scrubbers and combustion units, and sent to the 194 m stack. Leaching and recovery plants are sources of ammonia emissions from small stacks on the building roof or process equipment vents - ammonia is used in the process of nickel recovery from the reduced concentrate. The concentrate, removed of nickel, copper and cobalt is sent to the iron ore pelletizing plant, to produce pellets for marketing. In order to produce these pellets, the leached magnetite from the leaching plant is first dewatered to make filter cake which is then dried in two sintering machines. Gases from these machines are emitted via two 45 m stacks and four small stacks on the building roof. The two 45 m stacks are major sources of iron and total particulate emissions in the Basin until the plant shut down in April, 1980.

Nickel sulfide from the matte processing circuit is further processed in the Nickel Refinery to produce nickel in either powder or pellet forms. Nickel sulfide, precious metal intermediate products and refinery residues are first briquetted and then oxidized in two converters. The finished metal is further processed to produce metallic granules which undergo a carbonylation step, purification, decomposition and either pelletization or powderization. The most

significant source of emissions to the 194 m stack is from the converting step. The gases exhausted from the converters are passed through electrostatic precipitators in parallel prior to entering the flue leading to the stack. Even though converting is a batch process operated intermittently, these two converters are the major source of nickel emitted from the 194 m stack and also are also a source of low level emissions (mostly particulate and nickel) from the Nickel Refinery converter building.

INCO also operates three sulfuric acid plants, previously owned and operated by C.I.L., adjacent to INCO's Iron Ore Recovery Plant from which they receive sulfur dioxide. The sulfuric acid process involves oxidation of sulfur dioxide to sulfur trioxide on a catalyst and absorption of sulfur trioxide in absorption towers. Residual sulfur dioxide gas not converted to acid (conversion efficiency of about 93%) is vented to the atmosphere via the 194 m stack.

3.2.3 Falconbridge Limited Smelter Complex at Falconbridge

About 7100 standard cubic meters of gas at 120° - $160^{\circ}C$ are emitted from this stack every minute. The stack receives off-gases from the Falconbridge smelter operations including smelting and converting as well as the off-gases from the adjacent sulfuric acid plant. Prior to entering the stack the process gases pass through an electrostatic precipitator for the removal of the major portion of entrained particulates.

The Falconbridge smelting process was changed in 1978, hence the emissions from the plant should be considered in the two periods, before and after this change. Since 1978, two lines have been installed at the smelter, each containing a fluid bed roaster and an electric furnace, replacing the sintering machines and blast furnaces of the old process. The off gases from the roasters are cleaned of particulates in cyclones and electrostatic precipitators, cooled, and sent to an acid plant for the conversion of sulfur dioxide to sulfuric acid.

The calcine from the roasters are fed to electric furnaces for smelting. Emissions from the furnaces are first passed through cyclones and electrostatic precipitators and then sent to the stack. The furnace matte is sent to converters for further removal of iron and sulfur. There are four converters of which three are operated at anyone time. The off-gases from the converters are treated by electrostatic precipitators and then directed to the stack.

3.3 Emissions

The most significant source of air pollution in the Sudbury Basin is the 381 m stack at the INCO Metals Copper Cliff smelter. Depending on the type of pollutant, this source may contribute anywhere from 50% to over 80% of all emissions in the Basin. The only exception is copper, which is emitted in comparable quantities from other sources as well. In order of emission magnitude, the other sources of significant pollution in the area are the INCO 194 m IORP stack from its nickel refinery-iron ore recovery plant complex, Falconbridge 93 m stack and finally ventilators and windows which emit unconfined emissions from INCO's main smelter building at Copper Cliff.

Emissions of selected major pollutants from the measured sources in the Sudbury area are shown in Table 1. Maximum, average and minimum emissions, are shown wherever available. Emissions of sulfur dioxide from the INCO 381 m stack have been measured on a continuous basis since 1978, and were shown to change proportionately with the level of production. The emissions of particulates, iron, nickel and copper from the INCO 381 m stack shown in the table are considered the best estimates of yearly emissions. They were calculated from linear correlations between the measured emissions of sulfur dioxide and these other species such that they correspond to annual sulfur dioxide emissions. Emissions during shorter periods in any of the nine years studied could be either smaller or larger, depending on production. Emissions from the other sources in Table 1 were measured in shorter periods and are in some cases based on the results of one test only.

About 78% of all sulfur dioxide and 77% of sulfuric acid emissions are exhausted from the INCO 381 m stack; for total particulates the corresponding

contribution from this source is 75%, while the contributions to metal emissions are at 37-55% except for lead and arsenic which are mostly emitted from this source.

Up to April of 1980, when the pellet plant associated with the iron ore recovery process was shut down, INCO's two 45 m stacks were significant sources of particulate and iron emissions in the Basin. The best available emissions data are based on a single testing campaign on only one of the stacks. Hence, due to the paucity of data for this source, the emission rates presented in Table 1 were not included in the average emissions from the Sudbury Basin. This source is not expected to resume operation.

Emissions of oxides of nitrogen and hydrogen chloride were measured on two occassions at the INCO 381 m stack, and because they were small in comparison to sulfur dioxide and sulfuric acid the measurements were discontinued at this and other stacks.

Particle size is an important parameter in understanding the deposition of particulate pollutant and in determining the airborne part of the particulate emissions. Since most of the sources in the Sudbury Basin are controlled and the majority of particulates are removed by electrostatic precipitation at the source, it is expected, and confirmed by testing, that a large percentage of the particulates is less than 10 microns (um) in diameter, which constitutes, to a large extent, airborne particulate matter.

TABLE 1: AVERAGE YEARLY EMISSIONS OF MAJOR POLLUTANTS IN THE SUDBURY BASIN IN TONNES FOR THE PERIOD 1973 - 1981+

Source	Variation	Sulfur° dioxide	Sulfuric acid	Total Particulate	Iron	Copper	Nickel	Lead	Arsenic
INCO 381 m	Maximum	1,185,449	14,541	14,494	1,454	350	342	298	201
	Average	885,667	7,270	11,417	990	245	228	184	114
Stack*	Minimum	383,000	3,241	6,491	201	70	53	88	70
INCO 194 m	Maximum	104,390							
	Average	54,568	1,664	2,380	643	171	226	6	4
Stack	Minimum	18,980							
INCO Smelter	Maximum	16,000		755	90	312	40	0.8	0.1
	Average	12,000	88	586	70	242	31	0.6	0.1
(Low Level)	Minimum	6,000		283	34	117	15	0.3	0.1
INCO Two 45 m Stacks	Average			(4,073)	(2,354)				
Falconbridge	Maximum	274,000							
93 m	Average	173,000	438	865	98	11	9.6	13.4	6.4
Stack	Minimum	88,000							
TOTAL	Average	1,125,235	9,460	15,248	1,801	669	500	204	125

+ Basis: 365 days x 24 hrs/day production.

* Oxides of nitrogen emissions expressed as NO_2= 3,281 tonnes

* Hydrogen chloride emissions = 530 tonnes

* Emissions of particulates, iron, copper and nickel from the 381 m stack are yearly values calculated from correlations with sulfur dioxide emissions. Emissions of sulfuric acid, lead and arsenic are average measured values.

** Emissions ceased in April, 1980. Emission rates not included in average.

° Except for INCO Smelter (Low Level), all sulfur dioxide emissions were obtained by mass balance calculations.

3.3.1 Sulfur Dioxide

A combination of measurements and mass balance was used to produce sulfur dioxide emissions from the major industrial sources in the Sudbury Basin as shown in Table 2. Emissions from the INCO 381 m stack are mass balance values as reported by the company and they generally agree with the yearly average of the measured values to within 1-2%. As far as other emissions are concerned, the Falconbridge and INCO 194 m stack data were obtained by mass balance, while the low level emissions were obtained from measurements done in 1978 and 1979, and prorated to other years on the basis of production.

TABLE 2: YEARLY EMISSIONS OF SULFUR DIOXIDE FROM MAJOR INDUSTRIAL SOURCES IN THE SUDBURY BASIN IN THOUSAND TONNES

Source / Year	INCO 381 m Stack*	INCO Smelter Low Level++	INCO 194 m Stack*	Falconbridge 93 m Stack* +
1973	1,171	14	104	274
1974	1,126	16	74	258
1975	1,141	16	40	195
1976	1,163	15	41	191
1977	1,069	15	52(55)**	200
1978	535	8	24	117
1979	383	6	19	88
1980	733	11	66	123
1981	650	9	64	114
Average	885	12	54	173
% of total	78	1	5	16

* Determined from mass balance calculations.

\+ There were no direct measurements of Falconbridge low level emissions; however, they can be taken as approximately 2% of the smelter emissions.

++ Determined from measurements in 1978 and 1979 and prorated to other years on the basis of production.

** Determined from stack measurements.

For INCO, shutdowns and/or labor strikes in 1978 and 1979 were responsible for the low emissions in the Basin in those years. SO_2 emissions for 1980 and 1981 from the INCO 381 m stack reflect more stringent emission requirements imposed by the Ministry in 1980 which were met as a result of reduced production. With respect to emissions from the Falconbridge smelter, the levels were reduced as of 1978 largely as a result of a process change (installation of fluid bed roasting-electric furnace smelting - sulfuric acid manufacture). However, summer vacation shutdowns and lower production levels also contributed to the lower emissions presented in Table 2. In other respects, the tabulated emissions should be regarded as representative of each source.

With 78% contribution to the total emissions of sulfur dioxide in the Sudbury Basin, the 381 m stack is the largest single emitter of sulfur dioxide in the area. The accuracy of total sulfur dioxide emissions from the Basin depends to a large extent on the accuracy of these 381 m stack emissions, and it is for this reason that they have been measured on a continuous basis since 1973. The continuous emission monitoring installation for sulfur dioxide was verified through extensive testing in 1973, when it was demonstrated that the system was accurate to within $\pm$ 10%.

The low level emissions from the Copper Cliff smelter building were measured by INCO personnel in a series of tests at various vents, windows, and small stacks on the roof of the building. No similar measurements were done at the other INCO buildings or the Falconbridge smelter. The tests at INCO were specially designed and executed such that the measured emissions from the single process units selected for measurements as representative of a number of similar units in the same building were used to calculate the total emissions from

the building. Emissions shown in Table 2 were prorated to average yearly production rates of bessemer matte and blister copper. From among the individual processes, the largest contribution to these low level emissions of sulfur dioxide is made by the copper converters which account for about 41% of the total low level sulfur dioxide emissions, followed by the nickel reverberatory furnaces at 25%, the copper flash furnace at 17%, and the nickel converters at 8%. Miscellaneous sources account for about 9% of the total low level SO_2 emissions (INCO, 1981).

Sulfur dioxide emissions of the INCO IORP stack are based on the results of several tests of limited duration. Only in the case of the Nickel Refinery were the emissions prorated to correspond to the average production rate in 1977. These Nickel Refinery emissions are intermittent and are a result of approximately three "converter heats" per day, each heat lasting about four and a half hours. The emissions during a particular heat changed from a low of 5% to a high of 60% of the total emissions for the heat. Emissions from the sulfuric acid plants are continuous and are dependent on production. Emissions from Iron Ore Recovery Plant are sometimes subject to rapid fluctuations. The fluctuations were so large during testing that some doubts about the validity of tests and the meaning of the obtained results were expressed.

The Falconbridge 93 m stack is the second largest sulfur dioxide emitter in the Sudbury Basin, contributing on average about 16% of the total, over the nine years studied, as indicated in Table 2. These emissions have been computed from mass balance by company staff. In 1979 they were also measured over a short period, and the measured emissions were compared with the mass balance

values and found to be 49% higher. The Falconbridge plant emissions are variable due to the batchwise operation of the converters, and possibly variable efficiencies of the sulfuric acid plant, which both release off-gases to the 93 m stack.

3.3.2 Total Particulates

Most of particulate emissions in the Sudbury Basin are from the INCO 381 m stack. The 381 m stack emissions as shown in Tables 1 and 3 were obtained from a linear correlation between the particulate and sulfur dioxide emissions measured in the period from 1973 to 1981, such that they correspond to yearly average emissions of sulfur dioxide. Hence the estimated values do not correspond only to those process conditions which prevailed during the measurement tests, they also represent the best available average particulate emissions from this source. Emissions of total particulates from the INCO 381 m stack were measured in two or more tests every year from 1973 -1980. The lower particulate levels since 1978 relate to the concurrent lower SO_2 emission from the Copper Cliff smelter. Since about 75% of the total particulate emissions in the Sudbury Basin are due to the 381 m stack, any variation in these emissions will have a significant effect on the overall emissions of total particulates as well as the other particulate pollutants emitted in the Basin.

The low level particulate emissions as shown in Table 3 were also normalized with respect to production, however, in this case only one set of measured values from INCO's 1978-1979 testing program was available. Consequently, the calculated emissions shown in the table are less accurate than those for the 381 m stack. No such normalization was done for any other source listed in Table 3, and the indicated emissions from these sources were obtained from only one set of tests. From among individual smelting processes, the largest contributor to the low level particulate emissions from the smelter are

TABLE 3: AVERAGE YEARLY EMISSIONS OF TOTAL PARTICULATES IN TONNES FROM MAJOR INDUSTRIAL SOURCES IN THE SUDBURY BASIN FROM 1973 TO 1981.

Source / Year	INCO 381 m Stack	INCO Smelter Low Level Emissions	INCO 194 m and two 45 m Stacks	Falconbridge 93 m Stack
1973	12,166	650		
1974	14,144	730		
1975	14,299	755		
1976	14,494	721		
1977	13,763	703	2,380*	
1978	8,057	387		
1979	6,491	283	4,064**	865
1980	10,096	548		
1981	9,241	497		
Average	11,417	586		
Standard Error of Estimate	Sxy=4,588			

* These emissions were decreased in 1980 as a result of additional precipitator capacity at the nickel refinery plant flues.

** Emissions from two 45 m stacks not applicable after April 1980, due to plant shutdown.

the copper converters accounting for 64-70% of the total, followed by the nickel reverberatory furnaces at 9-11%, the nickel converters also at 9-11%, the multiple Hearth roasters at 9-11% and the copper flash furnace at 3%.

The INCO 194 m stack is the second largest industrial source of particulate emissions in the Basin. From among the three groups of plants contributing to the emissions from this stack, the acid plants are the least significant contributors of particulates, acccounting for about 8% of the total emissions, followed by the nickel refinery with 36% and the Iron Ore Recovery Plant with 56%. Comments on the continuity of emissions from the I.O.R.P. and the three acid plants, the intermittency from the nickel refinery plant, and on the production of these plants given in the discussion of sulfur dioxide emissions are also applicable to emissions of particulates. Emissions from the INCO 194 m stack have also been reduced since 1980, when additional precipitators were installed at the nickel refinery flues. However, the paucity of emissions data from the nickel refinery flue leading to the 194 m stack since the installation of additional precipitator capacity does not permit an accurate assessment of the degree of reduction effected. Nonetheless, it is anticipated that the reduction was substantial but further testing is required for confirmation. Emissions from the two 45 m stacks ceased in April 1980, when the pellet plant was shut down.

Particulate emissions from the Falconbridge 93 m stack were measured in 1973 and 1979. The results from 1973 are the only available emission data applicable to the old process at the Falconbridge plant and they suggest fairly high emissions at 19.2 tonnes per day. Unfortunately, since these measurements were done at only one point of the stack cross-section and were short in duration, their accuracy cannot be considered satisfactory. A more detailed measurement program was executed in 1979, when the new process was on line. The particulate emissions measurements obtained were much lower at 2.37 tonnes per day.

3.3.3 Trace Metals

Emissions of metals in the Sudbury Basin follow the trend established for particulates and are indicated in Table 1. On the average, the largest source of nickel, lead and arsenic emissions is the INCO 381 m stack, followed by the INCO 194 m stack, the Falconbridge 93 m stack, and INCO's Copper Cliff smelter building. However, in terms of particulate composition, the 194 m stack is a very significant source of copper and nickel. Even in terms of absolute quantities, this source used to emit almost as much of these two metals as the 381 m stack prior to the installation of additional precipitation capacity at the nickel refinery in 1980. Another significant source of copper is INCO's Copper Cliff smelter building, contributing about 37% of all copper emissions in the Basin. Iron was mainly emitted from INCO's two 45 m stacks until the pellet plant shutdown in 1980.

Not all metals were determined in all emissions measurements for the Sudbury source. However, the major species which, on the average, exceeded both one percent content of total particulate, and the emission rate of 10 kg h^{-1} from the 381 m stack over the nine-year period from 1973 to 1981, were quantified at all sources. Their emissions rates are shown in Table 4.

The iron, copper and nickel emissions shown in Table 4 were calculated from the correlation with sulfur dioxide, while lead and arsenic emissions were averaged from three or more valid emission measurement tests.

TABLE 4: AVERAGE EMISSIONS OF FIVE MAJOR METALS FROM INCO 381 M STACK IN KILOGRAMS PER HOUR

	Iron*	Copper*	Nickel*	Lead	Arsenic
1973	127	31	29	21	11
1974	163	39	37	29	10
1975	166	39	38	23	23
1976	169	39	39	12	15
1977	156	37	35	18	8
1978	52	14	12	10	-
1979	23	8	6	-	-
1980	89	22	21	34	10
1981	73	19	17	-	-
Average	113	28	26	21	13

* Emissions calculated from regression lines.

3.3.4 Sulfuric Acid

There are difficulties inherent in the determination of sulfuric acid in emissions from mineral processing. Consequently, a possibility exists that some of the measured emissions, with the exception of acid plants, are in error. This possibility was recognized after detailed analysis of test data, which were not always consistent with either theoretical expectations or other measurement programs. In most instances, inconsistencies were traced to improper sampling conditions and low sampling temperatures which allowed condensation of sulfuric acid on particulates and, hence, possible formation of artifact sulfates. The calculated emissions could have been underestimated. There are no similar interferences in the acid plant emissions, and these emissions can be considered accurate.

Depending on the source, acid emissions account for 0.4 to 3.0 percent of the total sulfur dioxide and acid emissions. At the INCO 381 m stack and the Falconbridge 93 m stack emissions, these percentages range from 0.4 to 1.4,

while in the INCO's 194 m stack, the percentage is higher at about 3%. The largest source of acid emissions is the 381 m stack, contributing about 77% to the total of 25.9 tonnes of acid per day from all major sources in Sudbury, as indicated in Table 1.

3.3.5. In-plume Particle Sizing and Emissions Rate Measurements

3.3.5.1 Falconbridge Stack Plume

In March and September, 1979, two airborne studies were carried out in the 93 m smelter stack plume of the Falconbridge Nickel Mines Ltd. at Sudbury, Ontario to determine particulate size distributions and pollutant emission rates. (Report ARB-TDA-57-80, Chan et al., 1982a)

The objectives of the work were to obtain information on the size distribution of various particulate constituents of the plume and to determine emission rates of these pollutants. The former objective was very important for (i) estimating particulate deposition rates (deposition velocity being a function of particle size); (ii) identification of the origin of ambient pollutants by comparing sizing results obtained at the plume and ground levels; and (iii) assessment of potential health effects which are a function of particle size.

It was found that particulates measured in the Falconbridge plume can be classified into 2 categories according to the mass median diameter (MMD) -coarse particles (MMD $>$ 2.5 um): Fe, Cu, Ni, Al and Mn; and fine particles (MMD $<$ 2.5 um): Pb, Zn, Cd, As, SO_4 and NH_4. The major emittant from the stack was $SO_4^=$. The chemical data, coupled with the sizing data, suggest that the sulfate collected was primarily in the form of sulfuric acid. Other pollutants which were emitted in relatively high quantities as measured in these

studies were Fe, Pb, Cu, Al, As and NO_3^-. A large temporal variability was noted, which can mostly be accounted for by process variation.

3.3.5.2 INCO Stack Plumes

In September, 1979 and February, 1980, airborne studies were carried out in the INCO 381 m smelter stack, and Iron Ore Recovery Plant (IORP) stack plumes, to determine the size distribution of the plume particulate constituents, and their emission rates, (Report ARB-TDA-62-80, Chan et al., 1982 b).

It was found that in the 381 m stack plume Fe, Cu, Ni, Al, Mg and Mn are predominately in the coarse particles, while Pb, Zn, As, SO_4, NH_4 and Se are predominately in the fine size range. On one day of atypical emissions (Feb. 5, 1980), when particulates were visually observed to be settling out near the stack (particulate fallout incident), mass median diameters (MMD) of most species were found to be greater than on other days. A relatively large variation of the particle emission rates for some trace metals was observed from the INCO 381 m stack. The major emittants were SO_4, Si, Fe, Pb, Ni As and Zn.

In the case of the IORP stack emissions, particulate size appeared to depend on the operating conditions in the Copper Cliff Nickel Refinery (CCNR). When only the IORP roaster/kiln off gases or sulfuric acid plant tail gases are emitting, the plume consitutents can be classified into coarse particles (Fe, Cu, Ni, Al and Cd) and fine particles (SO_4 and NH_4). In general, the metal particulates appear to be smaller when the CCNR as well as IORP and acid plants are in operation, whereas the reverse applies to SO_4 and NH_4. The size distribution of IORP emittants differs quite significantly from that of the INCO 381 m stack. Mass median diameters of Fe, Cu, Ni, Al and Cd are lower at IORP compared to those of the 381 m stack, whereas those of Pb, Zn, Cd, As, SO_4 and

NH_4 show the reverse pattern. The major emittants from IORP were SO_4, Fe, Ni, Cu, and Pb. It is interesting to note that the IORP stack emissions of Fe and Ni could be comparable or even higher than the corresponding values from the 381 m stack. Emissions of SO_4 and SO_2 from the IORP stack occur predominantly during the "blow" phase of the top blown rotary converter at the CCNR while those of Cu and Ni occur mostly during the "charge" phase. It should be noted that, with the installation of additional electrostatic precipitators treating the off gases from the top blown rotary converters, the particulate emissions are expected to have been considerably reduced. Emissions of Fe are quite uniform throughout the 3 different phases of the CCNR converter operation and the background IORP and acid plant operation.

4. REGULAR MONITORING PROGRAMS

In order to determine the ambient concentrations and fate of pollutants deposited through wet and dry mechanisms, and to provide data for model validation, monitoring programs were carried out over the period 1978-1980. In the following sections, descriptions of these programs and their major results are presented.

4.1 Wet Deposition Monitoring Program

4.1.1 Background of the Precipitation Monitoring Activities

The Air Resources Branch first became involved in precipitation monitoring in the Sudbury area in the early seventies. This early participation consisted of providing funds for the operation of a comprehensive bulk deposition network from 1972 to 1976. The network was designed and managed by Professor J.R. Kramer of McMaster University in Hamilton, Ontario, and the results of this work have been presented elsewhere (Kramer, 1973, 1975 and 1976).

In 1976, precipitation chemistry monitoring techniques had advanced to a point where long term bulk deposition sampling was considered unsatisfactory for measuring wet-only deposition. Funding of the bulk monitoring network ended at that stage and plans were made to install a wet-only deposition monitoring network as part of the Sudbury Environmental Study. The initial installation of a monthly wet-only sampling network took place in the summer and fall of 1977 and operation began in December 1977. The full implementation of the network was completed in mid-1978. The purpose of this cumulative sampling network was to monitor the long term wet deposition field out to a radius of 150 km from Sudbury.

In June 1978, a second deposition monitoring network was installed and put into operation. The sampling protocol in this network differed from that of the cumulative network in that it measured daily deposition on days of precipitation, rather than monthly wet-only deposition. Since most of these samples corresponded to precipitation events, the network was called the Sudbury Environmental Study event precipitation monitoring network. Sampling stations were predominantly located within 50 km of the Sudbury area smelters.

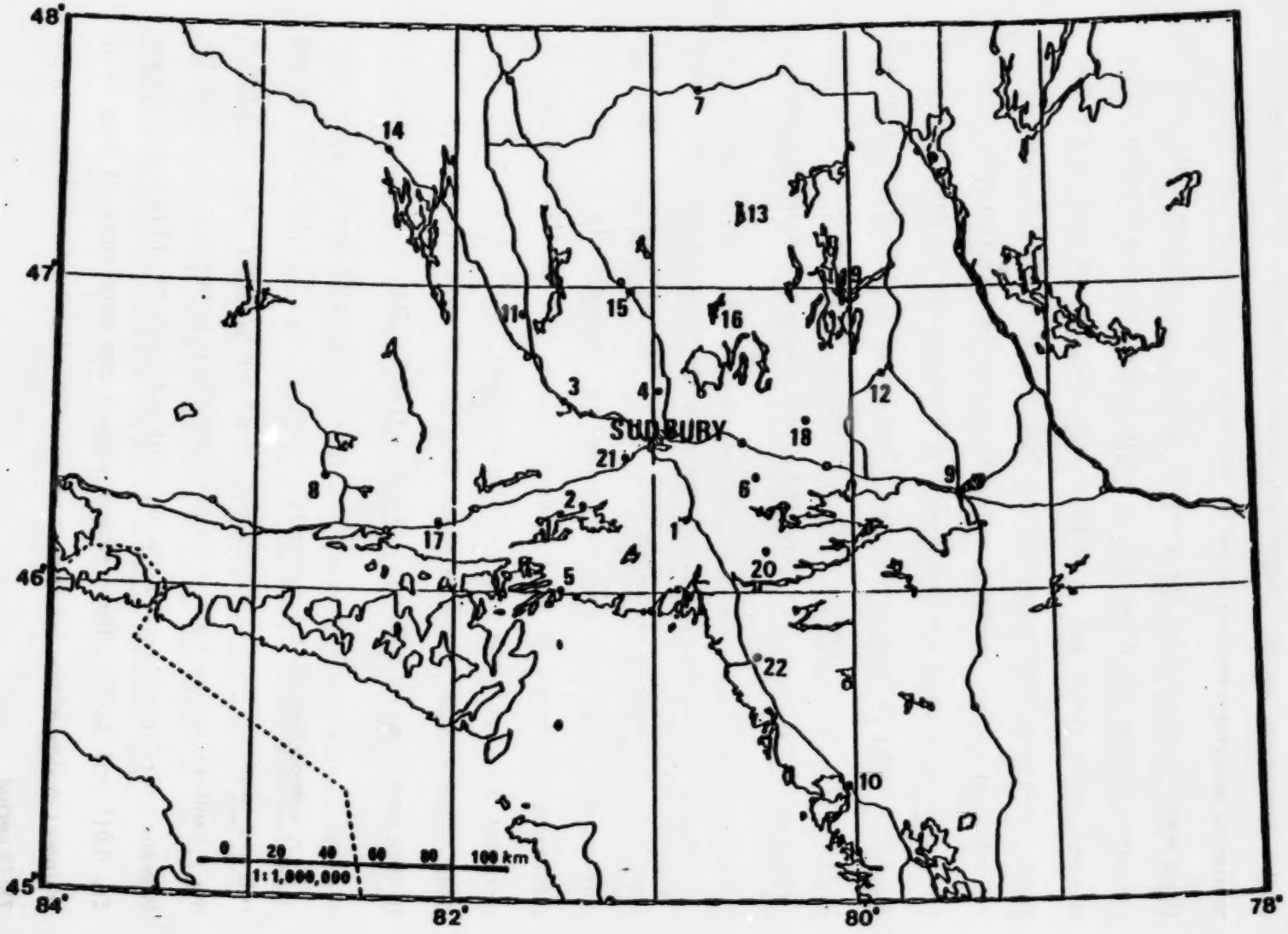
Both networks were operational until the end of the Sudbury Environmental Study field program in May, 1980. Details of the two networks are given in Reports ARB-04-82-ARSP and ARB-05-82-ARSP (Chan et al., 1982 c,d).

4.1.2 Cumulative Precipitation Sampling Network

The objectives of the SES cumulative network were two-fold:

1. To determine the impact of the local smelter sources on the long term wet deposition pattern of selected chemical species in the Sudbury area.
2. To provide wet deposition data for the development and verification of mathematical models of precipitation scavenging in the Sudbury area.

Figure 2 is a map of the network stations. At eighteen sites, Sangamo wet-only samplers were used. At four remote sites (Halfway Lake, Florence Lake, Graveyard Lake and Chiniguchi Lake) where line power was not easily accessable, battery-operated Aerochem Metrics Samplers were employed. Samples were collected on a monthly period (except during the period of July -



STATIONS

1. Burwash
2. Lake Panache
3. Windy Lake
4. Hanmer
5. Killarney
6. St. Charles
7. Cowganda
8. Elliott Lake
9. North Bay
10. Parry Sound
11. Halfway Lake
12. Marten River
13. Florence Lake
14. Ramsey
15. Graveyard Lake
16. Chiniguchi
17. Massey
18. River Valley
19. Bear Island
20. Noelville
21. Lively
22. Portage Lake

Figure 2: SES Cumulative Precipitation Sampling Network

September, 1978 when semi - monthly samples were collected), and were analysed for the concentration of acids and acid-related ions (sulfate, nitrate, ammonium), a number of trace metals (copper, nickel, zinc, iron, lead, chromium and cadmium), and other substances having contributions from soil and other origins (aluminum, calcium, magnesium, potassium, sodium, chloride, fluoride). Statistical analyses were carried out on the data. Concentration and deposition fields were constructed for the above substances, and assessed in the light of concurrent smelter operations. It is of special interest that the larger of the two smelters, INCO (which has an emission rate of sulfur and most of the trace metals considered here typically more than ten times greater than that of Falconbridge) was not operating, either due to maintenance shutdowns or labor disputes during most of the first study year (Falconbridge shutdown: July 1 to August 21, 1978; INCO shutdown: July 17 to August 27, 1978 and INCO strike: September 16, 1978 to June 7, 1979). Thus comparison of the two periods June 1978 -May 1979 and June 1979 -May 1980 yielded information on smelter impact.

During the lifetime of network operation the observed pH values ranged from 3.5 - 5.4, with a geometric mean of 4.1 for the entire network. The corresponding ranges (and geometric means) for concentrations of some other substances of interest, in mg l^{-1}, were: sulfate, 18.0 -0.3 (3.49); nitrate (as nitrogen), 3.0 - 0.3 (0.60); ammonium (as nitrogen), 3.1 - 0.01 (0.34); iron, 1.4 - 0.006 (0.068); copper, 1.1 - detection limit (d.l) (0.003); nickel, 0.079 - d.l. (0.002); lead, 0.067 - d.l. (0.011); and zinc, 0.31 -0.001 (0.010).

A comparison of the geometric means of the 78/79 and 79/80 periods referred to above, for all stations, gave: pH, 4.1 (78/79) and 4.2 (79/80); and in mg l^{-1} sulfate, 3.4 and 3.4; N-nitrate, 0.6 and 0.6; N-ammonium, 0.3 and 0.4; Fe, 0.06 and 0.07; Cu, 0.003 and 0.004; Ni, 0.001 and 0.002; Pb, 0.013 and 0.009; and Zn, 0.011 and 0.009. These results suggest the importance of long range transport in view of the fact that an extensive shutdown/strike took place in the 78/79 period.

H_f (free hydrogen ions) are strongly correlated with H_t (total hydrogen ions). Strong acids accounted for, on average, 70% of the total acid contents. H_f is better correlated with SO_4 than with NO_3. The correlation between NH_4 and SO_4 as well as NH_4 and NO_3 suggested that these species are chemically associated.

The precipitation concentration and wet deposition fields for the 1978/79 and 1979/80 periods showed the greatest impact of smelting activities to be for copper and nickel. A second group of trace metals (lead, zinc, chromium and cadmium) showed only a minor smelter impact. Results for the other substances examined (H^+, $SO_4^=$, NO_3^-, NH_4^+, Fe, Al, Mg^{++}, Ca^{++}, K^+, Na^+ and Cl^-) apparently were largely governed by non-smelter-related phenomena, such as long range transport into the study area, and contributions of local wind-blown dust or vehicular traffic. Since the event network data suggest that the smelter contribution to the wet deposition of these substances is generally less than 20% of the total in the Sudbury Basin (see below), any increment due to smelting activities is evidently masked by the inherent "noise" in the long term data (due to precipitation variability, sampling and analytical errors, contributions from local non-smelter sources and long range transport, etc.).

4.1.3 Event Precipitation Sampling Network

The objective of the SES event network was to quantify the relative contribution of the local smelter emissions from INCO and Falconbridge to precipitation quality and wet deposition of acids, major ions and trace metals in the Sudbury area. However, due to constraints of suitable sites and operators, the final network was designed primarily to assess the impact of the INCO source on the local environment. Figure 3 is a map of the event sites.

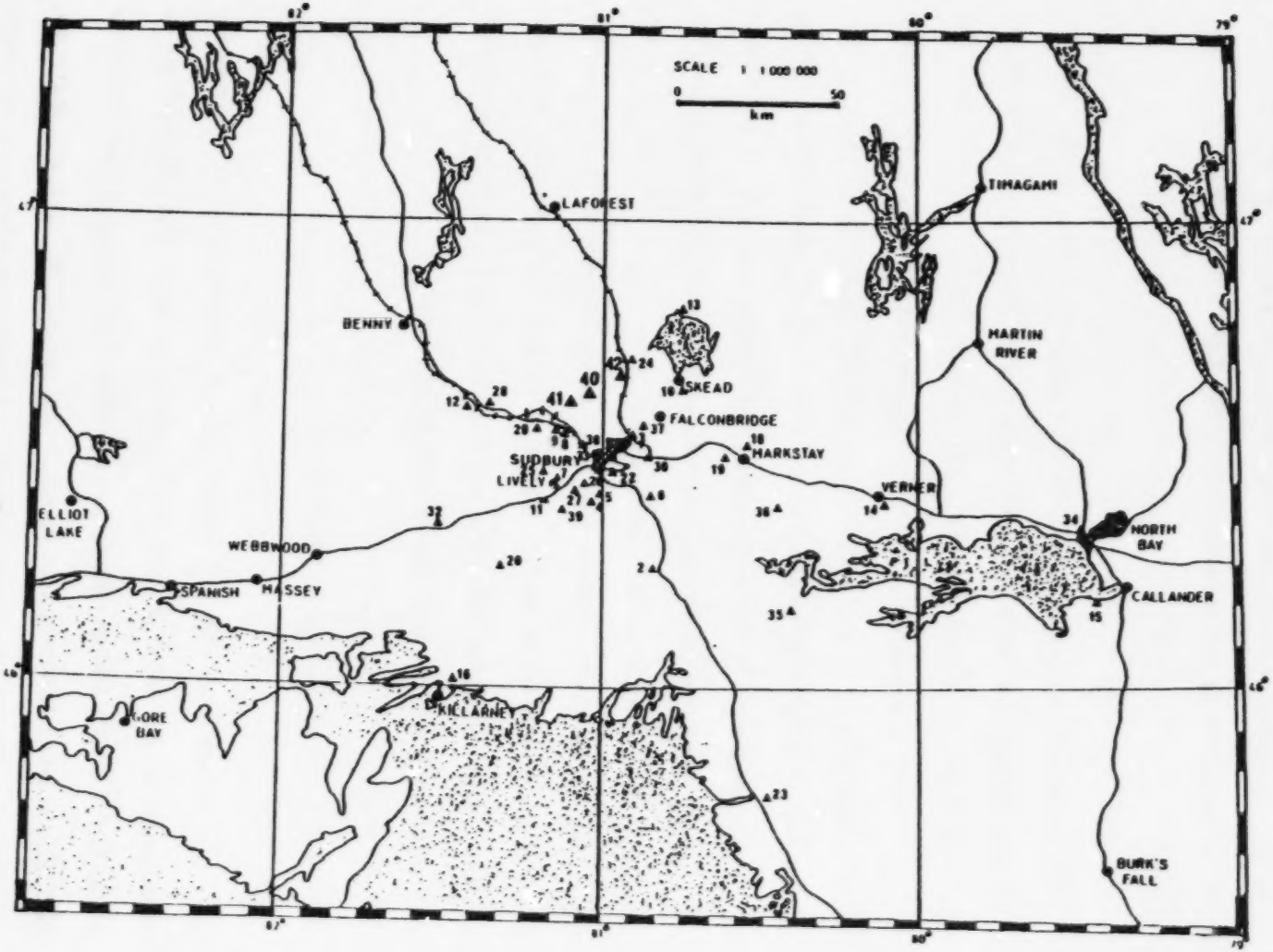


Figure 3: SES Event Precipitation Sampling Network

An analysis of the impact of the Sudbury smelter emissions on the Sudbury area using data from approximately 180 rain and snow events during the period mid-1978 to mid-1980, with precipitation samples collected upwind and downwind of both INCO and Falconbridge, was carried out. Of primary interest were two questions:

(1) What is the fate of the smelter emissions during precipitation events, i.e., how efficiently are they, on average, removed from the atmosphere, and how far from the source can the smelter effect be detected during storms in the Sudbury area?

(2) What is the relative contribution of the local and more distant (i.e. due to long range transport) sources to the local precipitation quality and deposition pattern?

Statistical analysis of the two-year data base was performed. Furthermore, the data were stratified according to the type of meteorological frontal passage, and whether or not the samples were influenced by the plume. From the analysis, the following conclusions were made:

The most acidic sample of the 2515 samples collected had a pH value of 3.4. The most alkaline one had a pH of 7.2. Most of the precipitation acidity can be attributed to H_2SO_4 and HNO_3. In this study, maximum SO_4 and N-NO_3 concentrations were 29.3 and 14.1 mg l^{-1}. Geometric mean SO_4 and N-NO_3 concentrations were respectively 2.8 and 0.5 mg l^{-1} suggesting that sulfuric acid is 1.6 times more important than nitric acid to acidity.

Maximum concentrations (in mg l^{-1}) of trace metals observed were: Fe = 3.9, Cu = 2.5, Ni = 0.9, Pb = 0.5, Zn = 1.7, Al = 2.3, Cr = 0.1, and Cd = 0.03. Most of the mean values were less than or equal to 0.01 mg l^{-1}.

Background precipitation concentrations associated with cold fronts were usually lower compared to those of warm fronts. Concentrations of the soil-derived constituents in winter precipitation were generally lower than that in summer precipitation.

Precipitation concentrations of SO_4 were higher in the summertime, whereas those of NO_3 were higher in the wintertime. This observation may be a consequence of different emission conditions, and oxidation and scavenging properties of SO_x and NO_x in the two seasons. Because of the compensating contribution of SO_4 and NO_3 to acidity, it was noted that the resultant acid concentrations were comparable in the two seasons.

Precipitation concentrations of species such as H_f, SO_4, NO_3, and trace metals which are found in sub-micron particles and have a contribution due to long range transport, were in general higher with trajectories from the S and SW sectors. This supports the observations regarding relative concentrations during warm and cold frontal passages.

With the exception of copper and nickel, most of the wet deposition in the Sudbury area (within a radius of 40 km) can be attributed to sources other than the local smelters. Long range transport from sources to the south is implicated for many parameters, notably acidity and the acid-precursors, sulfate and nitrate, because significantly higher background precipitation concentrations occur in warm, than in cold, frontal storms. The former usually enter the study area from south of Sudbury.

Nevertheless, a definite influence of the smelters on the local downwind precipitation quality can be detected for almost all of the substances

known to be emitted, the contribution due to INCO being considerably larger than that due to Falconbridge, in qualitative agreement with their respective emission rates. For example, average downwind precipitation copper and nickel concentrations were found to be an order of magnitude higher than background values in INCO's case. In many cases, this smelter influence can be detected to distance of more than 40 km from the source.

Most particulate constituents (acids, sulfates, trace metals) are scavenged quite efficiently from the smelter emissions during both rain and snow storms, almost total removal occuring within the Sudbury area for some trace metals (e.g. copper). The percentage of the total emitted sulfur thus removed is much lower, mainly because this sulfur is largely in the form of sulfur dioxide, which is subject to a low precipitation scavenging efficiency.

During precipitation events, the INCO smelter contributes on average 70% of the total copper and nickel wet deposition within 40 km, and less than 20% of the total for other trace metals and sulfur.

Table 5 summarizes the results, for wet deposition during precipitation events, for some of the substances emitted by the INCO smelter. Information for Falconbridge is considered to be considerably less accurate (due to much poorer network coverage around the Falconbridge smelter, and possible interferences from the larger INCO smelter's emissions), and will not be presented here.

TABLE 5: AVERAGE WET DEPOSITION OF INCO EMISSIONS WITHIN A 40 KM RADIUS OF THE SMELTER PER PRECIPITATION EVENT

	Emitted (kg)	Deposited (kg)	% Emissions Removed	% INCO Contribution to Total Wet Deposition
H_f*	4.5×10^2	1.4×10^2	32	6
S	5.2×10^5	3.4×10^3	0.7	8
Fe	7.1×10^2	4.8×10^2	68	20
Cu	2.6×10^2	2.7×10^2	100	69
Ni	3.5×10^2	1.3×10^2	36	67
Pb	2.1×10^2	0.7×10^2	33	14
Zn	0.55×10^2	0.5×10^2	93	12
Al	3.9×10^2	1.8×10^2	80	8
Cd	0.16×10^2	0.04×10^2	23	28
Cr	0.52×10^2	0.01×10^2	2.3	8

* Free hydrogen, calculated from pH measurements.

In connection with the above results, two facts should be pointed out. Firstly, the smelter impact on deposition, indicated in column 5 of Table 5, applies only to the level of smelter emissions (column 2) that occurred during the study period which was from mid-1978 to mid-1980. Any change in emission rates is expected to cause a corresponding change in the smelter impact. Secondly, the percentage of smelter emissions removed (column 4) is computed only for periods when precipitation was actually occurring. These constitute about 10% of the total time, with various dry deposition processes providing the only removal pathway during periods without precipitation.

Scavenging of plume constituents was not uniform throughout the year. For the acid and sulfur compounds, the scavenging seems to be more efficient in the summertime, whereas in the case of trace metals (except Pb, Cr and Zn which are in the fine-particle size range), the reverse seems to be true. All scavenging coefficients were typically in the order of 10^{-4} to 10^{-5} s^{-1}.

4.2 Dry Deposition Monitoring Program

In order to assess the ambient concentration and dry deposition rate of various pollutants emitted by the INCO and Falconbridge smelters, an airborne particulate matter (APM) monitoring network was set up using high volume (HiVol) samplers, and occasionally Andersen impactors (for particle sizing work), in the Sudbury area. The Sudbury Environmental Study HiVol air sampling program operated from July, 1978 to May 1980, with the following objectives:

(1) To quantify the contribution of local smelter emissions to the dry deposition field in the Sudbury area.

(2) To obtain air quality data on potentially toxic pollutants in the Sudbury area.

(3) To provide data for the verification of computer models developed to assess the fate of locally emitted pollutants.

Details of the HiVol program are given in Report ARB-12-81-ARSP (Chan et al. 1982e). Direct measurement of atmospheric dry deposition is extremely difficult, and no method presently exists that is suitable for routine field use. In 1977, a special study was attempted to directly measure SO_2 deposition rate at the INCO 381 m stack plume with COSPEC (correlation spectrometer) instrumentation. The phenomenon was so complicated and the technique was not sensitive enough to yield satisfactory results (Ward and Jain, 1979). An alternative, commonly-used approach has been to determine the ambient concentration of the particular substance of interest (be it in the gaseous or particulate form), and then to estimate the deposition flux from the product of concentration and a "deposition velocity" (the magnitude of which can be determined, although for some substances there are large uncertainties in the quantity). This latter approach was taken in this study.

Estimates of dry depositon rates were made both by detailed meteorological and air quality data analysis, and mathematical modelling (Ellenton, 1982). With the former approach, the aim was primarily to determine the relative impact of smelter emissions on the total dry deposition of sulfur and trace metals in the Sudbury Basin as a whole. Mathematical modelling was used to obtain a more detailed picture of the dry deposition field in the Sudbruy area, and dry deposition rates at particular receptors. The modelling work, which is described in more detail in Section 6.3, is still in progress.

Due to constraints of site availability and resources, the final ambient concentration monitoring network consisted of eight sampling sites (up to a distance of 50 km from the source). Six of these were in the south and southeast quadrants of the two smelter sources and they were downwind of the smelter sources characterized by one of the more dominant wind directions. One of the remaining two sites, Panache, was located in the southwest quadrant as a background monitoring site. The other one, Ash St., within the city of Sudbury, was located to measure both the effects of smelter emissions and urban activities on local air quality. The site location information is given Figure 4.

The General Metal Works Model GMWL 2000H High Volume Air Sampling System and Whatman 40 filter were used in this program. A three-day per week schedule was chosen with Sundays, Tuesdays and Thursdays as the principal sampling days. Twenty-four hour sampling was done from 0000 to 2400 hours EST.

The results reported here are based on the ambient concentration monitoring data for sulfur dioxide (continuous monitor measurements by the Northeastern Region of MOE), particulate sulfate, nitrate and ammonium, and trace metals (Hi-Vol measurements) together with particle sizing measurements, both at ground-level and within the INCO and Falconbridge smelter plumes, of sulfate and various metals

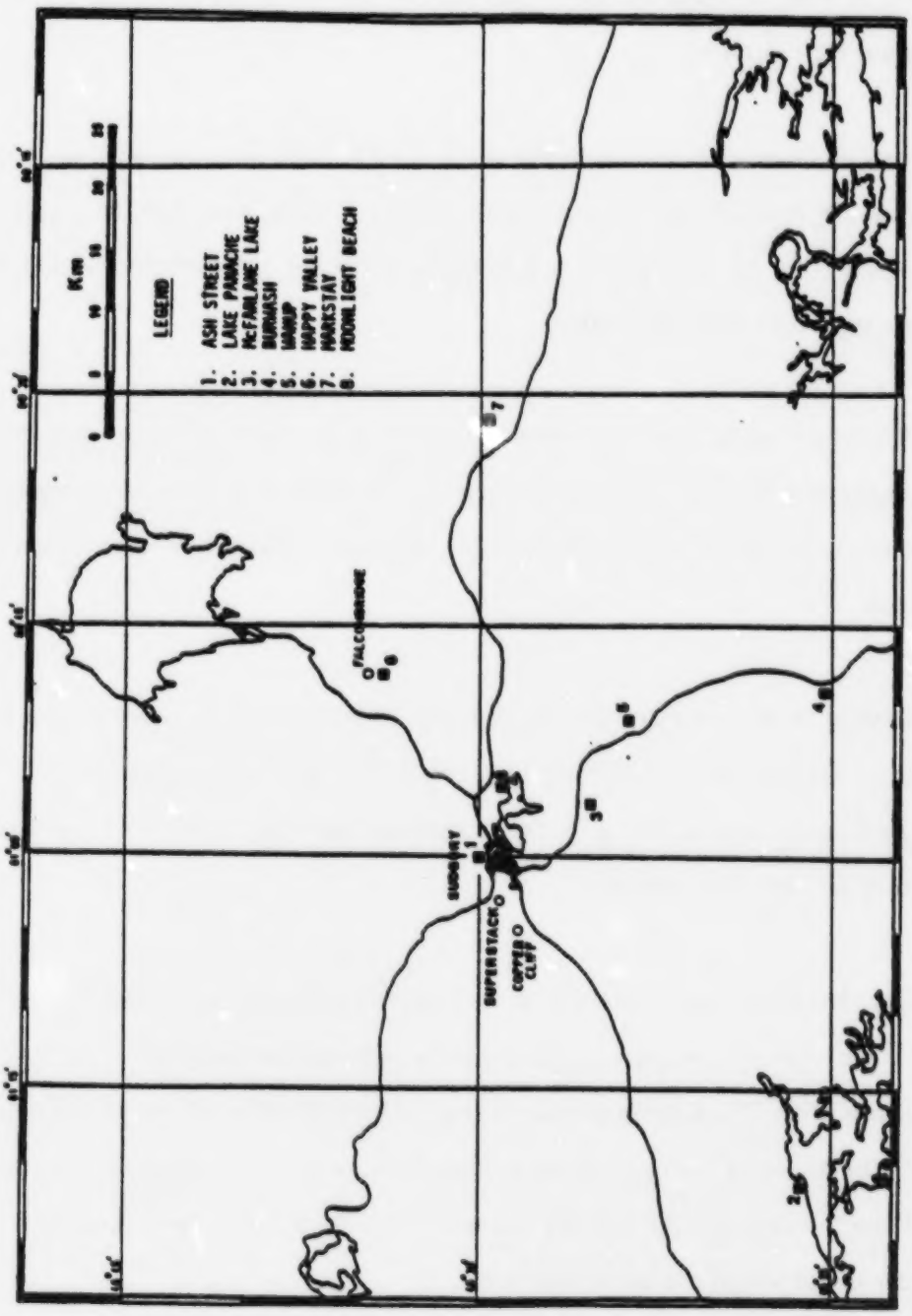


Figure 4: SES HiVol Sampling Network

(the latter measurements were needed to obtain deposition velocities for these substances). A detailed meterological analysis, together with ambient air concentration information, allowed a distinction to be made between samplers impacted by smelter emissions and those exposed to background air. The following conclusions were drawn:

The geometric mean concentrations (ug m^{-3}) over the two years were found to be: SO_2=12.7, $SO_4^=$=2.6, N-NO_3^- = 0.16, N-NH_4^+ = 0.54, Fe = 0.29, Ni = 0.005, Pb = 0.04, Zn = 0.02, Cd = 0.001, Al = 0.10 (lower limit only), Mn=0.003 (limited database) and Mg = 0.73 (limited database).

Statistical analysis of the data showed that SO_2 and SO_4 did not correlate highly, suggesting that the latter had a large contribution from long range transport. NH_4 and SO_4 however did correlate well, suggesting that they were chemically associated.

Ground level concentrations were found to be higher downwind of the INCO plume than the Falconbridge plume as expected from the relative source strengths. The parameters showing the greatest difference between plume and background concentrations were SO_2 and Ni.

Dry deposition was found to be a relatively inefficient removal mechanism for sulfur dioxide and substances predominantly in submicron particles (i.e. SO_4, Pb, Zn, Cd), less than 5% of the emissions being deposited within 40 km of the smelter sources. On the other hand, a higher proportion of the coarse particles (containing most of the airborne Fe, Al and Ni)- up to about 50% or more (long term average)- can be deposited within the same distance.

During the study period, the smelter contribution to the total dry deposition

within 40 km was greatest for sulfur (primarily due to SO_2) and nickel, making up 61% and 78% of the total respectively for INCO, and 36% and 40% for Falconbridge. The smelter contribution of the other metals examined (Fe, Pb, Zn, Cd and Al) was generally less than 20% of the total. Due to sampling problems, the corresponding figures could not be derived for copper, but results similar to those for nickel are expected, based on the available emission rate and particle size information.

Table 6 summarizes the results of the present investigation. It should be realized that the information on smelter impact on the dry deposition in the Sudbury area (i.e. the last column in Table 6) applies only to the level of emissions during the study period. Any change in the emission rates is expected to cause a corresponding change in the smelter contribution.

TABLE 6: DRY DEPOSITION OF INCO AND FALCONBRIDGE EMISSIONS WITHIN 40 KM OF THE SOURCES

	Parameter	Average Daily Emissions (Kg)	Estimated Dry Deposition (Kg)		% Emission Deposited	Smelter Deposition as % of Total*
			Average Smelter	Average Background		
INCO	SO_2	2.3×10^6	4.0×10^3	10.4×10^3	0.17	28
	SO_4	$4.9\ 10^4$	37	400	0.08	8.5
	total S	1.2×10^6	2.0×10^3	5.3×10^3	0.17	27
	Fe	1.6×10^3	280	1.3×10^3	17	18
	Ni	800	38	11	4.8	78
	Pb	480	0.75	4.1	0.16	15
	Zn	120	0.23	2.5	0.18	8.4
	Al	410	30	520	7.4	5.4
	Cd	37	0.007	0.15	0.02	4.5
Falconbridge	SO_2	2.9×10^5	3.2×10^3	10.4×10^3	1.1	23
	SO_4	4.7×10^3	19	240	0.40	7.4
	Total S	1.5×10^5	1.6×10^3	5.3×10^3	1.1	23
	Fe	100	140	1.1×10^3	140	11
	Ni	14	7.5	11	54	40
	Pb	37	1.4	5.0	3.8	22
	Zn	5.7	0.13	3.2	0.23	3.9
	Al	32	15	420	47	3.5
	Cd	12	0.006	0.15	0.05	3.9

* (INCO Deposition)/(INCO Deposition + Background Deposition) x 100%
or
(Falconbridge Deposition)/(Falconbridge Deposition + Background Deposition) x 100%

4.3 Relative Importance of Wet and Dry Deposition and Contribution of INCO Emissions to Total Deposition

Data reported in Tables 5 and 6 were combined to obtain information regarding (1) the contribution of INCO emissions to the total deposition, and (2) the relative importance of wet and dry deposition in the Sudbury area defined by a radius of 40 km. In this calculation, two assumptions were made: (1) precipitation occurs on every third day and (2) Cu dry deposition is similar to that of Ni. The results are summarized in Table 7. No similar comparison for the Falconbridge source was made because of uncertainties associated with the wet deposition results. However, it is expected that the contribution to the total deposition would be smaller than that of INCO reflecting their relative emission rates.

Note that whereas for sulfur and trace metals in large particles (Fe, Cu, Ni, Al) wet and dry depositions is similar, particles in the submicron size range (Zn, Pb, Cd) are primarily deposited by precipitation. As far as total deposition is concerned, the major smelter impact is on Cu and Ni. For most of the other substances examined, INCO contributes typically less than 20%.

The above results depend of course on the magnitude of the deposition velocity for submicron particles that is selected from the literature. It should be pointed out that this is currently a subject of considerable controversy, with some authors proposing values several times as large as those used here.

TABLE 7: A COMPARISON OF WET AND DRY DEPOSITION AND RELATIVE CONTRIBUTION DUE TO INCO AND BACKGROUND.*

Parameter	$\frac{(\text{Wet})_{\text{INCO}}}{(\text{Dry})_{\text{INCO}}}$	$\frac{(\text{Wet \& Dry})_{\text{Smelter}}}{(\text{Wet \& Dry})_{\text{Total}}}$	$\frac{(\text{Wet})_{\text{Total}}}{(\text{Dry})_{\text{Total}}}$
Sulfur	0.57	0.18	1.84
Fe	0.58	0.18	0.51
Cu	2.4+	0.7+	2.7+
Ni	1.1	0.72	1.3
Zn	85	0.12	53
Pb	29.2	0.14	34
Al	1.6	0.070	1.1
Cd	176	0.27	29

*Assuming precipitation occurs, on average, every third day. Results are average values for an area within 40 km of the source.

+Assuming similar dry deposition to that for Ni.

5. SUPPORTING STUDIES FOR MATHEMATICAL MODEL DEVELOPMENT

5.1 Meteorological Study

Quantitative determination of the fates of Sudbury emittants requires a detailed knowledge of the meteorological characteristics of the area. From September 1976 to September 1979 a specialized meteorological measurement program in the Sudbury area was carried out. The objective of the program was to obtain long term information on atmospheric stability and wind speed (and hence the capacity of the atmosphere to disperse the smelter emissions), as well as to provide a meteorological database for the development of mathematical models designed to assess the fate of locally emitted pollutants.

Details of the meteorological measurement program are given in Report ARB-009-81-ARSP (Vet et al., 1982a).

The program consisted of the measurement of wind speed, wind direction and temperature in the vertical using a pilot-balloon minisonde system. The balloon releases were carried out twice daily (once in the early morning and once in the early afternoon) under fair weather conditions. The balloons were tracked using dual theodolites. During the last year of the program, total incoming solar radiation measurements in the 300-2500 um wavelength region were also made as part of this program.

Data analysis was focussed on characterizing the meteorology of the Sudbury area during summer months (May to September) because it is during this period that most of the plume impingement episodes, and hence high ground level concentrations and dry deposition rates, occur. Impingements are governed

by the characteristics of the convective boundary layer (CBL), i.e. that portion of the atmosphere affected by the heating of the earth's surface.

Due to the large scale convective turbulence within the CBL, locally emitted pollutants released into the CBL behave in a manner known as looping, which ultimately results in the rapid mixing of the emissions throughout the entire layer, and high ground level concentrations near the stack.

The mean mid-day mixing height for the months of May through September was found to be approximately 1000 m above ground level. The mixed layer height was relatively constant through June, July and August and was slightly lower in May and September. The maximum mid-day mixing height measured during the program was 2328 m above ground level. The maximum for each month varied quite significantly. The greatest variability in mid-day mixing heights occurred in the months of May and June. The frequent mid-day average mixing heights of roughly 1000 m or more above ground level for the months of May through September indicate that the effectiveness of a tall stack for eliminating ground level concentrations is minimal during convective periods (because of plume looping). This is not the case however, during the night and during winter months, when inversions are generally below plume level and tend to keep the plume aloft thus preventing it from impinging at ground level. On the other hand, at these times low level emissions are trapped in stable air near the ground and can result in relatively high concentrations.

Mean mixed layer winds in the May-to-September period showed a predominant wind speed of 4 to 6 m s^{-1}. Westerly component winds had a frequency roughly four times greater than easterly component winds, and wind speeds associated with the two components were noticeably different. For the

period from May to September, the average mixed layer wind speed for westerly component winds was 6.4 m s^{-1} while that for easterly component winds was 3.8 m s^{-1}. The differences in both the frequency and speed of the mixed layer winds have major implications on local air quality and dry deposition. The upper level inversion above the mixed layer capping inversion had a mean mid-day potential temperature lapse rate of 3.3 °C km^{-1} over the study period.

The strong bias for westerly component mixed layer winds suggests that the dry deposition field for locally emitted pollutants should also be biased. Based on the wind direction frequency data, increased dry deposition would be expected in the northeasterly, easterly and southerly directions.

The indications (based on a small data base) of stronger wind speeds with westerly component winds also has a major impact on local air quality and dry deposition. It suggests that, on average, ground level concentrations and dry deposition, should be lower near the stack for westerly component winds than for easterly component winds.

Monthly mean values of total incoming solar radiation during mid-day hours (1100-1500 h), averaged from May to September were in the range of 600 to 800 W m^{-2}. Daily maximum values over a monthly period were 200 to 500 W m^{-2} greater than the corresponding monthly means. For days with known convective activity, the monthly means were 50 to 250 W m^{-2} greater than the mid-day means obtained using data from all days.

5.2 Special Studies

Special field studies were carried out to obtain specific information on plume chemistry and physics. Aside from the in-plume

emission rates and sizing experiments described in 3.3.5, two other types of studies were carried out and the results are summarized here.

a. Oxidation of SO_2 to SO_4 in the INCO 381 m stack plume

b. Turbulence and dispersion studies of the INCO 381 m stack plume

5.2.1 SO_2 To Sulfate Oxidation in the INCO 381 m Stack Plume

Atmospheric chemical transformations can have a significant effect on both the fate and the environmental impact of the emitted pollutants. The SO_2 to SO_4 oxidation rate in the 381 INCO stack plume had been studied by Lusis and Wiebe (1976) in September 1974 and June 1975. It was found that at distances close to the stack, sulfate accounts for 1.2 to 1.5% of the total sulfur and less than 10% of the total sulfur was in the form of sulfate even as far as 100 km downwind from the source. The conversion rate ranged from 0 to 7% per hour with an average of 1% h^{-1}. There was some indication of slight decrease in conversion rate with plume age, but no temperature or humidity dependence was observed.

Further investigations of the oxidation rate of SO_2 in the 381 m stack plume were carried out by the Ministry in September 1976 and February, March and June, 1977 (see Report ARB-TDA-60-79, Chan et al.1979 and Chan et al. 1980). It was found that particulate sulfur in the 381 m INCO stack plume appeared to be predominantly in the form of sulfuric acid, and comprised less than about 4% of the total plume sulfur, out to distances of about 100 km from the 381 m INCO stack.

These same investigations confirmed that the SO_2 oxidation rate in the INCO 381 m stack plume was low - typically, less than 0.5% h^{-1}. This rate applies to temperature and relative humidity ranges of -11 to 18°C and 34 to 87% and to plume ages less than 5 hours. Estimates of the oxidation

rate from the event precipitation chemistry network data suggest that the above figure is also representative of "wet" conditions.

5.2.2 Turbulence and Dispersion Studies

In June 1978 and August 1979, intensive field programs were carried out in the Sudbury area to study the dispersion of the INCO 381 m stack plume in the convective boundary layer (CBL), and to provide experimental data for the verification of a short term, short range fumigation model for the estimation of ground level concentrations of SO_2 due to this stack's emissions. Results are described in Report ARB-003-81-ARSP, Vet and Chan (1982b).

Airborne measurements were made of plume sulfur dioxide concentrations at various distances from the source. At the same time, ground-level measurements were made of atmospheric turbulence as well as sulfur dioxide within the fumigation area, and minisondes were used to determine wind speed and direction as well as the vertical temperature profile.

In both field studies, the height of the convective boundary layer was generally well-defined by a strong daytime capping inversion. Under this inversion the wind speed was relatively constant with height, but accelerated quickly above it. The potential temperature within the CBL was also relatively constant. The wind direction typically varied with height within the mixed layer but became roughly constant above it. The diurnal cycle of the mixed layer followed a relatively consistent pattern. In the morning, the mixed layer developed rapidly as it responded to the increase in solar flux and the consequent increase in heat flux. This rapid growth generally occurred from 0900 to 1300 hours. At 1300 to 1400 hours, the mixed layer reached its maximum height and remained relatively constant until approximately 1800 hours. The maximum

daily solar flux was reached at 1300 to 1400 hours. After the maximum was reached, the afternoon decline in solar flux had no apparent effect on the relatively constant mixed layer height.

Plume dispersion within the CBL is characterized by behaviour known as looping. On warm sunny days the INCO 381 m stack plume begins looping typically between 1000 and 1100 hours and stops roughly one to two hours before sunset. The initial impingement of individual plume loops usually occurs at a distance of 3 to 10 km from the stack and results in intermittent, high, ground level concentrations. Farther downwind, the plume becomes well-mixed in the vertical. Concentrations are not as high, and are less intermittent.

6. MATHEMATICAL MODELLING

Attempts were made to develop models in connection with the Sudbury Environmental Study to account for long and short range as well as long and short term observations. The following sections describe three models. Even though the state-of-the-art approach was used to understand the long term, short range measurements, the model is still under development and details will be reported later. Some of the initial results are given in Section 6.3.

6.1 Long Range, Long Term Model

A simple statistical model has been developed for estimating long-term concentrations of sulfur pollutants associated with long-range transport. The model consists of three components; transport and dispersion, scavenging and chemistry. Dispersion and wet scavenging is treated statistically. Dry deposition is treated by assuming loss at the ground through a dry deposition velocity. Chemistry is treated linearly. The model was used to estimate wet deposition of sulfur over a grid covering northeastern United States and Canada. The model estimates compare well to corresponding measurements of annual deposition, and the model has been applied to estimate the relative contribution of INCO and Falconbridge to the total sulfur deposition in Ontario and Quebec. (Report-ARB-36-81-SES, Venkatram et al., 1982).

Four emission scenarios were considered. The first was the base case, where INCO and Falconbridge's emissions were represented by the 1977 values, which are considered to be representative of the mid - 1970's - viz., 1,340,000 metric tonnes of SO_2. The second considered average annual emissions at their level during the 1978-1979 strike-shutdown period for both INCO and Falconbridge. The third scenario assumed emissions to be at maximum allowable as of December 1980 - i.e. 465 and 2500 short tons of SO_2 per day respectively

for Falconbridge and INCO. The final scenario assumed INCO's smelter SO_2 emissions to be at the maximum allowable as of January 1, 1983, as specified by the August 28th, 1980 Control Order - namely 1950 short tons per day. It was assumed throughout that emissions from all other sources except for Falconbridge, remained at their mid-1970 values. The maximum currently allowed rate, e.g. 465 short tons per day, was used for Falconbridge.

The model estimates show that sources in the Sudbury region contribute 5 - 30% of the total sulfur deposited during precipitation in most of north-central Ontario and western Quebec under typical mid - 1970's conditions. Near Sudbury the model predictions exceed 30%; however, close to the source the long range transport model is no longer applicable, because the model design is based primarily on large scale atmospheric flow characteristics. Although INCO's emissions dominated the wet deposition from the Sudbury sources, Falconbridge did contribute a significant amount (1-5%) of the total.

Sulfur dioxide emissions from the Sudbury area were greatly reduced by shutdowns and strikes during the 1978-1979 period (Scenario 2). The model estimates show a reduction in annual wet sulfur deposition to 2 - 20% of the total over approximately the same region of north-central Ontario and western Quebec.

The third scenario represents the maximum contribution of current Sudbury emissions to the long term average deposition of sulfur, since actual annual emissions are expected to be somewhat less than the annual values calculated from maximum daily emissions. The model results showed that the Sudbury region would contribute 3-25% of the deposition in north -central Ontario and western Quebec under these conditions.

The results of the fourth simulation showed that the Sudbury emissions would contribute a maximum of 2-23% of the total sulfur deposition during precipitation in north-central Ontario and western Quebec. Reducing the model emissions for the Sudbury region from 1977 to projected 1983 levels decreased this area's contribution to long-term wet deposition in Muskoka-Haliburton by as much as 7% of the total 1977 wet deposition.

In general, the model indicates that wet sulfur deposition in central and northern Ontario and Quebec has a significant contribution from smelters in Sudbury, Wawa and Noranda, and that reducing emissions from Sudbury as indicated above would significantly reduce this region's contribution to the total deposition of sulfur during rain. The model also indicates that in spite of these reductions, Sudbury area emissions still would remain a major contributor to deposition in the non-industrial area of north-central Ontario and western Quebec.

Care must be taken in the interpretation of these results. The model results are estimates of long term wet deposition rates expressed as annual amounts and are not expected to compare well with measurements taken either near the emission sources or over short periods of time.

6.2 Short Range, Short Term Fumigation Model

Conventional "Gaussian type" dispersion models cannot predict ground level concentrations (g.l.c.) of pollutants associated with plumes emitted into the convective boundary layer. Most high glc's at Sudbury are associated with convective conditions. A model was therefore developed for this purpose. The required data inputs to the model are the climatology of the mixed layer height, solar radiation, mixed layer winds and the temperature structure above the mixed layer, and are described in Report AQM-AMB 1 (Venkatram, 1982).

The model was evaluated with ground level concentrations obtained in the field study described in Seciton 5.2.2. The model has also been evaluated for two separate data sets obtained in Maryland, US. Using a factor of two criterion to judge the accuracy of model predictions, it is observed that 80% of data obtained during Sudbury field experiment and 85% of the Maryland data meet this criterion. The factor of two criterion is commonly used in air pollution studies.

Due to the large buoyancy of the plume from the INCO 381 m stack, the effective emission height is about 800 m above ground. During most of the year the atmospheric boundary layer does not grow to this height and the plume is not brought down to the ground. However, during the daytime hours of the summer months, the boundary layer associated with surface heating by solar radiation grows to heights greater than 1000 m. The plume is then mixed down to the ground and high SO_2 concentrations can occur. Thus, in terms of local air quality, the emissions from the 381 m stack are a problem primarily during hot summer days.

It is noted that high ground level concentrations can sometimes be observed during night time at Sudbury, although these occurrences are rare. The model under consideration is applicable for day time convective conditions and should be restricted to that period.

The obvious application of the model is in supplementary emission control. Meteorological inputs to the model are predicted a few hours prior to the anticipated plume breakup time. The model is used to determine the emission rate which will ensure that the maximum expected concentration (predicted) will be below the local air quality standard. Cutbacks in emissions are implemented if an exceedance is likely.

6.3 Short Range, Long Term Model

The short range, long term model uses statistics of meteorology over several years in the simulation of transport and dispersion of pollutants. Ground level ambient concentration as an annual or seasonal average is computed for locations within a distance of about 100 km from the source of emission. Annual dry deposition is also calculated. This model is in the development stage. Preliminary comparison of calculated seasonal SO_2 concentrations with observed values have given encouraging results.

Simulation of concentration at any specific location involves the determination of three essential factors. These are: (i) the frequency with which the wind blows from each source to this location, (ii) the probability of plume impingement at the distance of the receptor from the source under varying meteorological conditions and (iii) concentration during impingement. Information used for these calculations includes statistics of wind direction frequency, wind speed and incoming solar radiation, plus emission strength and stack characteristics.

In order to generate meteorological statistics for the long term model, a year is viewed as being composed of 12 "average" months for which the meteorology has been averaged for several years. Each month is represented by an "average" 24 hour day.

Comparison of model computed SO_2 concentrations, as seasonal averages, with ıneasured values form 17 monitors in the MOE network for 2 summer and 2 winter seasons shows agreement within a factor of 2, for 80% of the values.

Dry deposition is caluclated as the product of concentration and deposition velocity, i.e., the rate of transfer to the ground. This is computed at each model hour and accumulated to give an annual value. Dry deposition

velocity of SO_2 is determined in the model as a function of wind speed, atmospheric stability, surface roughness and the resistance of soils and vegetation to the uptake of SO_2.

Since dry deposition is difficult to measure, there are no data of routinely monitored dry deposition of SO_2 for comparison with model values. Computed dry deposition due to Sudbury emissions shows a roughly elliptical pattern extending maximum values northeastward and minimum values to the northwest of Sudbury.

Further refinements in the calculations of SO_2 concentration and deposition are expected. Thus model results should be regarded as tentative at this time. Extension of the simulation capabilities to include sulfates and some metals is under way.

7. CONCLUSIONS

Based on several years of source sampling at the INCO and Falconbridge smelters, air and precipitation monitoring, a number of special field studies of dispersion and chemical reactions of the emissions, and mathematical modelling of smelter impact, both near the source ($\leq$ 40 km) and at further distances ($>$ 40 km), the atmospheric research activities of the Sudbury Environmental Study have resulted in the following conclusions:

- Based on stack tests carried out during the period 1973-1981, the best available estimates of the average yearly emissions, in tonnes, for the major pollutants are as follows (both INCO and Falconbridge sources are included): sulfur dioxide, 1,098,462; sulfuric acid, 9,460; total particulates, 15,248; iron, 1,801; copper, 669; nickel, 500; lead, 204; and arsenic, 125.

- The largest single source in the Sudbury Basin is the INCO 381 m stack, which emits 78% of all the sulfur dioxide and 77% of the sulfuric acid in the Sudbury area, and 75% of the total particulates. However, several other sources -notably the 194 m and 45 m stacks (this latter source ceased emitting in 1980) at INCO's Iron Ore Recovery Plant, as well as Falconbridge's 93 m stack are also very significant contributors. Some of the available data also suggest that low level emissions at the INCO smelter are significant sources of particulates, having high concentrations of copper.

- Measurements of the size distributions of the emitted particulates have yielded somewhat different results for each source sampled, but have in general shown that substances such as particulate sulfur ($SO_4^=$) and volatile metals (lead, zinc, arsenic) are in particles having mass median diameters less than 2.5 microns, while iron, copper and nickel are in particles larger than this (mass

median diameters of about 10 microns). Most of the emitted sulfate seem to be in the form of sulfuric acid.

- Extensive precipitation sampling and chemical analysis during the period from December 1977 to May 1980 showed a network average pH of 4.1 within about 100 km of the smelters, with individual samples having values ranging between 3.4 and 7.2. Long term geometric means of sulfate and nitrate (as nitrogen) were 2.8 and 0.5 mg l^{-1} respectively (there were some differences in the mean values obtained from the cumulative and event networks, due to different sampling methodologies and network spatial coverage), with individual samples showing maximum concentrations of 29 mg l^{-1} of sulfate and 14 mg l^{-1} N-nitrate respectively for specific events. The mean concentrations suggest that sulfuric acid is 1.6 times more important than nitric acid to acidty. Long term network average concentrations (in mg l^{-1}) for some of the trace metals of major interest were: iron (0.07); copper (0.003); nickel (0.002); lead (0.01); and zinc (0.01). However, in individual samples, concentrations an order of magnitude or more above these values were observed. Meteorological analysis usually showed such high values to be due to an impact of the smelter plume(s). Also, precipitation concentrations of many substances, notably acids and sulfates, were generally higher during warm frontal rather than cold frontal storms, indicating the impact of long range transport from industrial areas to the south on precipitation chemistry in the Sudbury Basin.

A comparison was made of the data from cumulative monthly precipitation chemistry samples during a prolonged shutdown of the INCO smelter (June 78 - May 79), with corresponding observations when the smelter was operating (June 79-May 80). The greatest impact of smelting activities was found to be for concentrations of copper and nickel, with only minor changes in the concentration patterns of lead, zinc, chromium and cadmium. No detectable differences between the two periods for the other substances examined (including acidity, sulfate and nitrate) were noted. Thus, for the latter group

of substances, any increment due to smelting activities is evidently masked by the inherent "noise" in the long-term data (due to precipitation variability, contributions from local non-smelter sources and long range transport, etc).

These results are consistent with conclusions based on a careful meteorological and chemical analysis of event precipitation samples. This analysis found that a definite influence of the smelters on the local downwind precipitation quality could be detected for almost all the substances known to be emitted, and that most particulate constituents (but not sulfur dioxide) are scavenged quite efficiently from the smelter emissions during both rain and snow storms. However, the INCO smelter, on average, was found to contribute less than 20% of the total Sudbury Basin wet deposition of sulfur, acidity and a number of trace metals, with the exception of copper and nickel, where the contribution is about 70% of the total wet deposition. The above values apply to the smelter production levels during the study period (mid-1978 to mid-1980). Any change in emission rates would probably cause a corresponding change in smelter impact. Due to network coverage constraints, there are large uncertainties in the results for the Falconbridge source.

- Estimates of dry deposition in the Sudbury Basin were made, based on ambient concentration and particulate size distribution measurements, and information relating particle size to deposition velocity in the literature. These indicated that for sulfur dioxide and substances predominantly in submicron particles (sulfate, lead, zinc and cadmium), less than 5% of the emissions are deposited within 40 km of the smelter sources, whereas for coarse particles (containing most of the iron, nickel and copper), 50% or more of the emissions are deposited within this distance. During the study period (July 1978 to May 1980), the smelter contribution to the total dry deposition within 40 km of the

source was the greatest for the total sulfur and nickel making up 27% and 78% of the total respectively for INCO, and 23% and 40% for Falconbridge. Due to sampling problems, results for copper were not obtained but are expected to be similar to those for nickel. The smelter contribution to the other metals examined (iron, lead, zinc, cadmium, aluminum) was generally less than 20% of the total dry deposition.

- Estimates of the INCO smelter contribution to the sum of the wet and dry deposition in the Sudbury Basin were also made. The major smelter impact was found to occur for copper and nickel, where the smelter contribution was about 70% of the total wet plus dry deposition within 40 km of the source. For most of the other substances examined (sulfur, iron, zinc, lead, aluminum, cadmium), the smelter contributed less than 20% of the total. Also, it was found that whereas for sulfur, and trace metals in large particles (iron, copper, nickel, aluminum), wet and dry deposition of the smelter emissions is of similar importance in the Sudbury Basin, particles in the submicron size range (zinc, lead, cadmium) seem to be primarily deposited by precipitation.

- The air sampling program yielded information on the ambient concentrations of sulfate, nitrate and a number of trace metals in the Sudbury area. Geometric mean concentrations (in micrograms per cubic meter), during the study period, were found to be: sulfate, 2.6; nitrate (as nitrogen), 0.16; ammonium, 0.54; iron, 0.29; nickel, 0.005; lead, 0.04; zinc, 0.02 and cadmium, 0.001. For the trace metals, the above values are somewhat biased towards high values, because only a selected number of samples were analysed, including a preponderance of samples under the influence of smelter emissions. Meteorological analysis of the data showed that there was a definite elevation of most of the above constituents downwind of the smelters.

- A detailed meteorological investigation into atmospheric stability and wind speed and direction, as well as solar radiation, over the period September 1976 - September 1979, showed that during the months of May to September, mid-day mixing heights frequently exceeded 1000 m above ground level, causing plume looping from the INCO 381 m chimney. This indicates that this tall stack is of limited effectiveness for eliminating high concentrations at ground level. This is not the case, however, during the night and during winter months, when inversions are generally below plume level, and tend to keep the 381 m stack plume aloft.

- A mathematical air quality model was developed, which can be used to predict ground level concentrations resulting from plumes emitted into the convective boundary layer, and is of potential value for supplementary emission control. The model was validated using data from two intensive field programs (carried out in June 1978 and August 1979) examining the dispersion of the INCO 381 m stack plume in the convective boundary layer, as well as data from studies of other tall stack plumes.

- A number of studies were undertaken to study the oxidation of sulfur dioxide to sulfates in the INCO 381 m stack plume, covering a range of ambient temperatures (-11 to 18°C) and relative humidities (34 to 87%). Oxidation rates were found to be low (typically, less than 0.5% h^{-1}) and estimates based on precipitation chemistry data suggest similar values under "wet" conditions as well.

- The Ministry's statistical long range transport model was used to estimate the contribution of the Sudbury smelters to sulfur wet deposition in Ontario and Quebec. For smelter emissions representative of those in the mid-1970's (1.3 x 10^6 metric tons of sulfur dioxide per year), these sources were estimated to

contribute 5 to 30% of the total sulfur deposited during precipitation in north-central Ontario and western Quebec. Falconbridge contribution amounts to 1 to 5% of the total. Other scenarios were also examined, including the shutdown/strike period in 1978-1979 and that which assumes INCO and Falconbridge emissions to be at the maximum allowable as of December 1980 and January 1983. In the former case, the model estimates show a reduction in annual wet sulfur deposition to 2-20% of the total. The corresponding values for the latter two cases were 3 to 25% of the total wet deposition, and 2 to 23% of the total wet deposition respectively. The model suggests that in spite of reductions in the wet sulfur deposition due to the Sudbury smelters, brought about by the August 28th, 1980 Control Order, these sources would still remain a major contributor to wet deposition of sulfur in the non-industrial areas of north central Ontario and western Quebec.

REFERENCES

Chan, W.H., R.J. Vet, M. A. Lusis, J.E. Hunt and R.D.S. Stevens (1979) "Airborne Investigations of the INCO and Falconbridge Stack Plumes, 1976-77" Report ARB-TDA-60-79, Air Resources Branch, Ontario Ministry of the Environment.

Chan, W.H., R.J. Vet, M.A. Lusis, J.E. Hunt and R.D.S. Stevens (1980), "Airborne Sulfur Dioxide to Sulfate Oxidation Studies of the INCO 381 m Chimney Plume", Atmospheric Environment, 14 1159-1170.

Chan, W.H., R.J. Vet, G.B. Skelton and M.A. Lusis (1982a) "Size Distribution and Emission Rate Measurements of Particulates in the 93 m Falconbridge Smelter Stack Plume, 1979", Report ARB-TDA-57-80, Air Resources Branch, Ontario Ministry of the Environment.

Chan, W.H., R.J. Vet, M.A. Lusis and G.B. Skelton (1982b) "Size Distribution and Emission Rate Measurements of Particulates in the INCO 381m Chimney and Iron Ore Recovery Plant Stack Plumes, 1979-80", Report ARB-TDA-62-80, Air Resources Branch, Ontario Ministry of the Environment.

Chan, W.H., R.J. Vet, C.U. Ro, A.J.S. Tang and M.A. Lusis (1982c) "Precipitation Quality and Wet Depositon in the Sudbury Basin: Sudbury Environmental Study Cumulative Precipitation Network Results" Report ARB-04-82 -ARSP, Air Resources Branch, Ontario Ministry of the Environment.

Chan, W.H., C.U. Ro, R.J. Vet, A.J.S. Tang and M.A. Lusis (1982d), "An Analysis of the Impact of Smelter Emissions on Precipitation Quality and Wet Deposition in the Sudbury Area: Sudbury Environmental Study Event Precipitation Network Results". Report ARB-05-82-ARSP. Air Resources Branch, Ontario Ministry of the Environment.

Chan, W.H., R.J. Vet, C.U. Ro, A.J.S. Tang and M.A. Lusis (1982e), "An Analysis of the Impact of Smelter Emissions on Atmospheric Dry Depositon in the Sudbury Area: Sudbury Environmental Study Event Airborne Particulate Matter Network Results" Report ARB-12-81-ARSP, Air Resources Branch, Ontario Ministry of the Environment.

Ellenton, G. (1982) Ontario Ministry of the Environment Report, to be published.

Fitz, L. (1978), "Report and Recommendations of Provincial Officer for INCO Limited Operations in the Regional Municipality of Sudbury", Ontario Ministry of the Environment, Northeastern Region report.

INCO (1981), "Feasibility of Controlling Low Level Emissions from the Copper Cliff Smelter Complex", INCO Process Technology, Project No. 047. 21, December 15.

Kramer, J.R. (1973), "Fate of Atmospheric Sulphur Dioxide and Related Substances as Indicated by Chemistry of Precipitation", McMaster University, Department of Geology Report.

Kramer, J.R. (1975), "Fate of Atmospheric Sulphur Dioxide and Related Substances as Indicated by Chemistry of Precipitation", McMaster University, Department of Geology Report.

Kramer, J.R. (1976), "Fate of Atmospheric Sulphur dioxide and Related Substances as Indicated by Chemistry of Precipitation". McMaster University, Department of Geology Report.

Lusis, M.A., and H.A. Wiebe (1976), "The Rate of Oxidation of Sulfur Dioxide in the Plume of a Nickel Smelter Stack", Atmospheric Enviornment, 10 793-798.

Ozvacic, V. (1982) "Emissions of Sulfur Oxides, Particulates and Trace Elements in Sudbury Basin" Report ARB-ERTD-09-82. Air Resources Branch, Ontario Ministry of the Environment.

Venkatram A., B.E. Ley and S.Y. Wong (1982). "A Statistical Model to Estimate Long-Term Concentrations of Pollutants Associated with Long Range Transport and its Application to Emissions from the Sudbury Region", Report ARB-36-81-SES, Air Resources Branch, Ontario Ministry of the Environment.

Venkatram, A. (1982), "Short Range Short-Term Fumigation Model for the INCO Superstack." Report AQM-AM8 1, Air Resources Branch, Ontario Ministry of the Environment.

Vet, R.J., S. Linauskas, W. Bardswick and W.H. Chan, (1982a), "Sudbury Environmental Study Meteorology Program", Report ARB-09-81-ARSP, Air Resources Branch, Ontario Ministry of the Environment.

Vet, R.J. and W.H. Chan (1982b), "Two Intensive Field Studies of Dispersion of the INCO 381 m Stack Plume in the Convective Boundary Layer", Report ARB-003-81-ARSP, Air Resources Branch, Ontario Ministry of the Environment.

Ward, T.V. and Jain, S (1979). "Remote Sensing Study to Determine the Downward Depositon of SO_2 from the INCO Smelter" Report MTR-78-8R. Submitted to Air Resources Branch, Ontario Ministry of the Environment by the Moniteq Limited.

Appendix 1

List of ARB/SES-related Publications

GENERAL

Sudbury Environmental Study - An Overview, W.H. Chan, M.A. Lusis and R.J. Vet, paper 80-52-4a, 73rd Annual Meeting of the Air Pollution Control Association, Montreal, Quebec, June (1980).

SOURCE AND SOURCE STRENGTHS

Acid, Particulate and Particle Sizing Sampling at INCO Superstack, Sept., 1976. Report ARB-TDA-39-77 (May, 1977).

Acid Particulate and Particle Sizing Sampling at INCO Superstack, June, 1977. Report ARB-TDA-53-78 (February, 1978).

Sulfur Dioxide, Sulfuric Acid, Particulate and Particle Size Determinations at Falconbridge Smelter Stack, August, 1979. Report ARB-TDA-40-80, by V. Ozvacic and J. McDonald.

Particle Size Determinations at the 380 m chimney, INCO Smelter, Copper Cliff, Ontario, Report ARB-TDA-43-80 (June, 1980).

Determination of the Extent of Particulate Stratification at the INCO 381 Meter Chimney at Copper Cliff, Ontario. Report ARB-TDA-58-80 by V. Ozvacic and J. McDonald. (1982)

Emissions of Sulfur Oxides, Particulates and Trace Elements in Sudbury Basin. Report ARB-ERTD-09-82 by V. Ozvacic (1982).

SPECIAL STUDIES

Airborne Investigations of the INCO and Falconbridge Stack Plumes, 1976-1977, W.H. Chan, R.J. Vet and M.A. Lusis, Report ARB-TDA-60-79 (May, 1979).

Airborne Sulfur Dioxide to Sulfate Oxidation Studies of the INCO 381 m Chimney Plume, W.H. Chan, R.J. Vet, M.A. Lusis, J.E. Hunt and R.D.S. Stevens, Atmospheric Environment, 14, 1159-1170 (1980).

Airborne Estimation of Particulate Emissions from Stacks: A Feasibility Study, W.H. Chan, R.J. Vet, M.A. Lusis, J.E. Hunt and R.D.S. Stevens, Atmospheric Environment, 14, 1201-1203 (1980).

Remote Sensing Study to Determine the Downwind Deposition of SO_2 from the INCO Smelter, T.V. Ward and S.C. Jain, Report MTR 78-8R. Submitted to Ontario Ministry of the Environment by Moniteq Ltd. (1979).

Size Distribution and Emission Rate Measurements of Metals and Sulfates Within A Smelter Plume, R.J. Vet, G.B. Skelton, W.H. Chan and M.A. Lusis, Paper 80-67.2, 73rd Annual Meeting of the Air Pollution Control Association, Montreal, Quebec, June (1980).

Report on An Ambient Air Quality Survey in the Sudbury Area, August, 1979, R. Chapman, Report ARB-TDA-67-80 (April, 1981).

Airborne Particulate Size Distribution Measurements in Smelter Plumes, W.H. Chan, R.J. Vet, M.A. Lusis and G.B. Skelton, Paper presented at the 3rd EPA Symposium on Advances in Particle Sampling and Measurement, Daytona Beach, Florida, October (1981).

Two Intensive Field Studies of Dispersion of the INCO 381 M Stack Plume in the Convective Boundary Layer, R.J. Vet and W.H. Chan, Report ARB-003-81-ARSP (1982).

Size Distribution and Emission Rate Measurements of Particulates in the 93 M Falconbridge Smelter Stack Plume, 1979, W.H. Chan, R.J. Vet, G.B. Skelton and M.A. Lusis Report ARB-TDA-57-80 (1982)

Size Distribution and Emission Rate Measrements of Particulates in the INCO 381 M Chimney and Iron Ore Recovery Plant Stack Plumes, 1979-80, by W.H. Chan, R.J. Vet, M.A. Lusis and G.B. Skelton Report ARB-TDA-62-80 (1982)

MONITORING NETWORKS

An Analysis of the Sudbury Environmental Study Network Precipitation Acidity Data, June-September, 1978, R.J. Vet, W.H. Chan and M.A. Lusis, Report ARB-TDA-84-79 (February, 1979).

An Analysis of the Impact of INCO Emissions on Precipitation Quality in the Sudbury Area, W.H. Chan, C.U. Ro, M.A. Lusis & R.J. Vet, Report ARB-TDA-35-80 (May, 1980).

Analysis of Precipitation Measurements in the Vicinity of a Nickel Smelter, C.U. Ro, W.H. Chan, M.A. Lusis and R.J. Vet, Paper 80-52. 4b, 73rd Annual Meeting of the Air Pollution Control Association, Montreal, Quebec, June (1980).

Impact of the INCO Nickel Smelter Emissions on Precipitation Quality in the Subury Area, W.H. Chan, C.U. Ro, M.A. Lusis and R.J. Vet, Atmospheric Environment 16 (4) 801-814 (1982).

Sudbury Environmental Study Meteorology Program, R.J. Vet, S. Linauskas, W. Bardswick and W.H. Chan, Report ARB-009-81-ARSP (1982).

An Analysis of the Impact of Smelter Emission on Atmospheric Dry Deposition in the Sudbury Area: Sudbury Environmental Study Airborne Particulate Matter Network Results, W.H. Chan, R.J. Vet, C.U. Ro, A.J.S. Tang and M.A. Lusis, Report ARB-012-81-ARSP (1982).

Precipitation Quality and Wet Deposition in the Sudbury Basin: Sudbury Environmental Study Cumulative Precipitation Network Results, W.H. Chan, R.J. Vet, C.U. Ro, A.J.S. Tang and M.A. Lusis, Report ARB-04-82-ARSP(1982).

An Analysis of the Impact of Smelter Emissions on Precipitation Quality and Wet Deposition in the Sudbury Area: Sudbury Environmental Study Event Precipitation Network Results, W.H. Chan, C.U. Ro, R.J. Vet, A.J.S. Tang and M.A. Lusis, Report ARB-05-82-ARSP (1982).

MODELING PROGRAM

Modeling of Dispersion from Tall Stacks, A. Venkatram and R. Vet, Atmospheric Environment 15 (9), 1531-1538 (1981).

Model Predictability with Reference to Concentrations Associated with Point Sources, A. Venkatram, Atmospheric Envionment, 15 (9), 1517-1522 (1981).

Short Range Short-Term Fumigation Model for the INCO Superstack, A. Venkatram, Report AQM-AMB 1 (1982)

A Statisical Model to Estimate Long-Term Concentrations of Pollutants Associated with Long Range Transport and Its Application to Emissions from the Sudbury Region, A. Venkatram, B.E. Ley and S.Y. Wong., Report ARB-36-81-SES (1982).

A Statistical Model to Estimate Long-Term Concentrations of Pollutants Associated with Long Range Transport, A. Venkatram, B.E. Ley and S.Y. Wong, Atmospheric Environment 16(2), 249-257 (1982).